Conjugated Block Copolymers for Opto-Electronic Functions

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Abstract

A novel block copolymer system containing a conjugated donor block (RO-PPV) and a conjugated acceptor block (SF-PPV) coupled by a non-conjugated bridge unit has been synthesized and characterized. While the donor block film has a strong PL emission at around 570 nm, and acceptor block film has a strong PL emission at around 590 nm, the PL emissions of -DBAB- block copolymer films were quenched by over 99%. Preliminary thin film electron microscopy studies revealed certain regular morphological pattern, possibly due to block copolymer microphase separation.

Keywords: Conjugated block copolymers, donor and acceptor blocks, opto-electronic and photovoltaic devices.

1. Introduction

It has been known that the donor (p-type) conjugated polymers help stabilize and transport the positive charges (holes), and acceptor (n-type) conjugated polymers help stabilize and transport the negative charges (electrons), thus photo induced electron transfer and charge separation observed in organic composites of donors and acceptors offered a potential organic molecular approach to high efficiency light harvesting or opto-electronic applications [1-7]. Such systems and devices have recently been demonstrated using polythiophene/CN-PPV bilayers [2], MEH-PPV/CN-PPV blends [3-4], MEH-PPV/C₆₀ bilayers [5] and blends [6], MEH-PPV/PS-C₆₀ di-block copolymers [7], etc.

In our recent approach, a conjugated donor block "RO-PPV" or (D) is coupled to a conjugated acceptor block "SF-PPV" or (A) via a short non-conjugated bridge unit (B) to form a -DBAB- type block copolymer system. In this system, the charge separation can be maximized since the interfacial area can be conveniently controlled via block copolymer segment size control. Every donor block can be built in a convenient reach of an acceptor block within an effective exciton diffusion range. On the other hand, the charge recombination between the donor and acceptor blocks at the backbone junction is hindered due to a non-conjugated bridge unit.

2. Results and discussion

Figure 1 shows the chemical structures and synthetic scheme of –DBAB-. Specifically, the donor block (D) is an alkyloxy derivatized polyphenylenevinylene or "RO-PPV", the acceptor block (A) is an alkyl-sulfone

D Excess B B-D-B A D-B-A-B
Excess B B-A-B D -D-B-A-B
RO

OR

D = Donor Block = "RO-PPV"

RO 2S

A = Acceptor Block = "SF-PPV"

R = C 2H₅, C₈H₁₇, C₁₀H₂₁ Y = C H₂PO(O C₂H₅)₂, CHO

OH C -O-(CH₂)_p O -CHO H₂N-R- NH₂

Fig. 1. Donor and acceptor block copolymer systems investigated.

Bridge Unit 1 = B

Bridge Unit 2 = B

derivatized polyphenylenevinylene or "SF-PPV". Two bridge units were studied, first one is a dialdehyde terminated bridge unit 1, and the second is a diamine terminated bridge unit 2. When bridge unit 1 was used, both donor and acceptor blocks were synthesized with terminal phosphate groups. When amine terminated bridge unit 2 was used, both donor and acceptor blocks were synthesized with terminal aldehyde groups. The synthesis of 2-ethyl-hexyl derivatized RO-PPV and SF-PPV conjugated blocks, and the synthesis of dialdehyde bridged –DBAB- have been recently presented [8-11]. The synthesized –DBAB- has been characterized by NMR,

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GPC, MALDI, thermal analysis, optical spectroscopy, electrochemical analysis, electrical conductivity, electron microscopy, etc [12]. In this paper, we present our recent photoluminescence (PL) and preliminary electron microscopic data of –DBAB- thin films.

Figure 2 shows thin film PL emission spectra of RO-PPV (D), SF-PPV (A) and -DBAB-. As we can see, the RO-PPV film has a PL emission maximum at about 570 nm, and the SF-PPV film has a PL emission maximum at about 590 nm. However, the density correlated PL emission of -DBAB- film was quenched by over 99% in comparison to donor and acceptor films. At the same time, ground state electron transfer between donors and acceptors in -DBAB- was not observed as the UV-VIS absorption of -DBAB- is roughly the simple overlap of donors and acceptors [9, 12]. Thus the PL quenching is mainly due to photo induced electron transfer between donor and acceptor blocks [13]. Preliminary atomic force microscopy (AFM) studies revealed certain regular morphological pattern in the -DBAB- film on a silicon substrate (Fig. 3, image area 7.5x7.5µm), and this may possibly be due to block copolymer microphase separation. Detailed microscopic studies are ongoing and will be reported in near future.

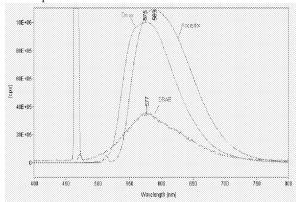


Fig. 2. PL emission spectra of D (RO-PPV), A (SF-PPV-I), and –DBAB- films. The spikes at 470 nm and 510 nm are due to film reflected excitation beam. The PL intensities (y-axis) are arbitrary for better view.

3. Summary and Conclusions

A novel –Donor-Bridge-Acceptor-Bridge- (-DBAB-) type conjugated block copolymer system has been synthesized. In comparison to pristine donor or acceptor blocks, the PL emissions of final -DBAB- block copolymer films were quenched by over 99%. Effective and efficient photo induced electron transfer and charge separation occurs due to the interfaces of micro phase separated donor and acceptor blocks. The system is very

promising for variety high efficiency light harvesting applications.

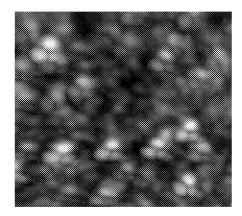


Fig. 3. AFM image of a -DBAB- film on a Si substrate (non-contact mode)

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